

Introduction

Graphitized carbon black (GCB) is a common sorbent used for reducing matrix interferences when extracting per- and poly-alkyl substances (PFAS) from complex environmental matrices, such as sediments, soils, sludges, and nonpotable water. For certain regulated methods, the use of GCB is mandated, such as in the US Department of Defense guidelines (DOD QSM 5.1/5.3). Ideally, the GCB should remove matrix interferences that affect quantitation and method robustness while not significantly reducing PFAS recovery or adding interferences. In this paper, the use of GCB for the extraction of PFAS compounds from environmental extracts is studied in detail. The sorbents' effectiveness for the removal of matrix interferences will be presented for a variety of environmental samples and PFAS compounds.

Matrices and extraction materials

Two matrices were selected for this experiment: sedge peat and sandy loam.

Matrix	Supplier (p/n)
Dark reed sedge peat	Michigan Peat Company (5440)
Sandy loam	Supelco (CLNSOIL3)

Consumables that were used were for extraction were compatible with PFAS analysis.

Description	Agilent (p/n)
Bond Elut Carbon, 250 mg, 6 mL, 30/pk	12102201
Vac Elut SPS 24 Manifold with collection rack for 10 x 75 mm test tubes	12234003
Collection rack and funnel set for 12 or 15 mL conical tubes, for Vac Elut SPS 24 Manifold	12234027
Centrifuge tubes and caps, 15 mL, 50/pk	5610-2039
Polypropylene autosampler screw top vials	5191-8151 and 5191-8150

Extraction procedure

Weigh 2 g of soil into a 15 mL centrifuge tube.

Add 10 mL of 2% ammonium hydroxide in methanol (first extraction).

Vortex for 10 minutes, then centrifuge at 9000 rpm for 5 minutes.

Decant extract into a clean 15 mL centrifuge tube.

Add 3 mL of 2% ammonium hydroxide in methanol to soil (second extraction).

Vortex for 10 minutes, then centrifuge at 9000 rpm for 5 minutes.

Add the second extract to the first extract in the 15 mL centrifuge tube.

Rinse the Bond Elut Carbon SPE with 10 mL 2% ammonium hydroxide in methanol and discard.

Pass the extract over the cartridge and collect eluent into a clean 15 mL centrifuge tube.

Rinse the Bond Elut Carbon SPE with 3 mL of 2% ammonium hydroxide and collect eluent.

Evaporate the 15 mL extracts under a gentle stream of nitrogen at 55-60 °C until dry.

Reconstitute in 1 mL 80:20 methanol:water and analyze.

Analysis

Extracts were analyzed by LC/Q-TOF adapted for PFAS analysis.

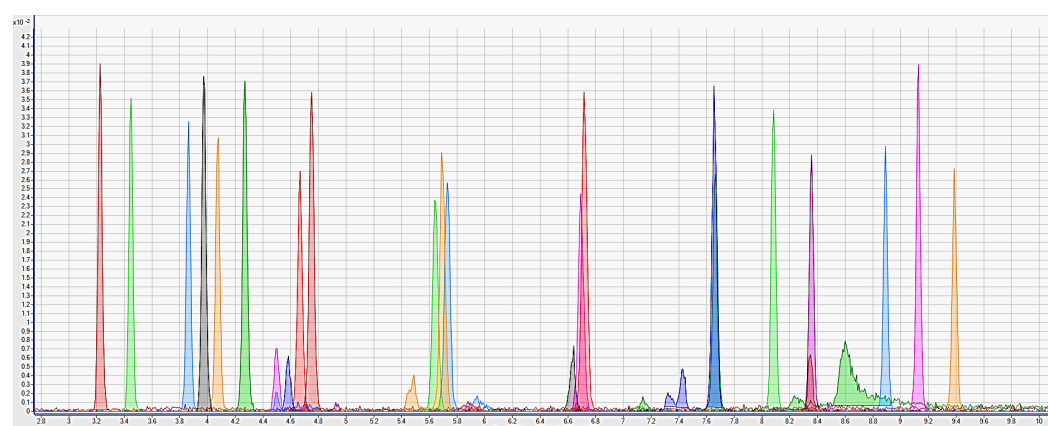
Parameter	Value			
LC	Agilent 1290 Infinity II LC			
Analytical Column	Agilent ZORBAX RRHD Eclipse Plus C18, 2.1 x 150 mm, 1.8 μm (p/n 859700-902)			
Delay Column	Agilent InfinityLab PFC delay column (p/n 5062-8100)			
Injection Volume	5 μL			
Mobile Phase	A. 20 mM ammonium acetate in water B. MeOH			
Gradient	Time (min)	A%	B%	Flow (mL/min)
	0.00	95	5	0.300
	1.00	95	5	0.300
	30.00	60	100	0.300

Parameter	Value
MS	Agilent 6545 quadrupole time of flight LC/MS with Agilent Jet Stream ESI source
Source Parameters	
Polarity	Negative
Drying Gas	230 °C, 4 L/min
Sheath Gas	250 °C, 12 L/min
Nebulizer Gas	15 psi
Capillary Voltage	2500 V
Nozzle Voltage	0 V

Results and discussion

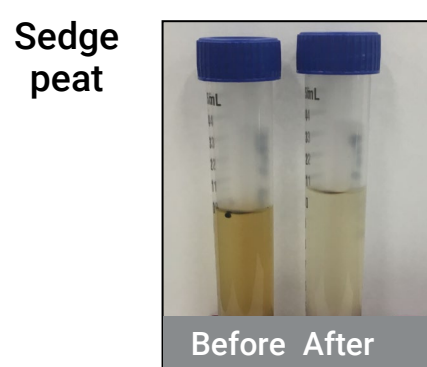
LC/Q-TOF analysis

A typical exact mass extracted ion chromatogram for 25 PFAS standard at 1000 ng/L is shown below. The sharp symmetrical peaks are from the analytes in the injected standard. The broad asymmetrical peaks are the system peaks separated from the analytical peaks by the delay column.



Pigment removal with Bond Elut Carbon SPE

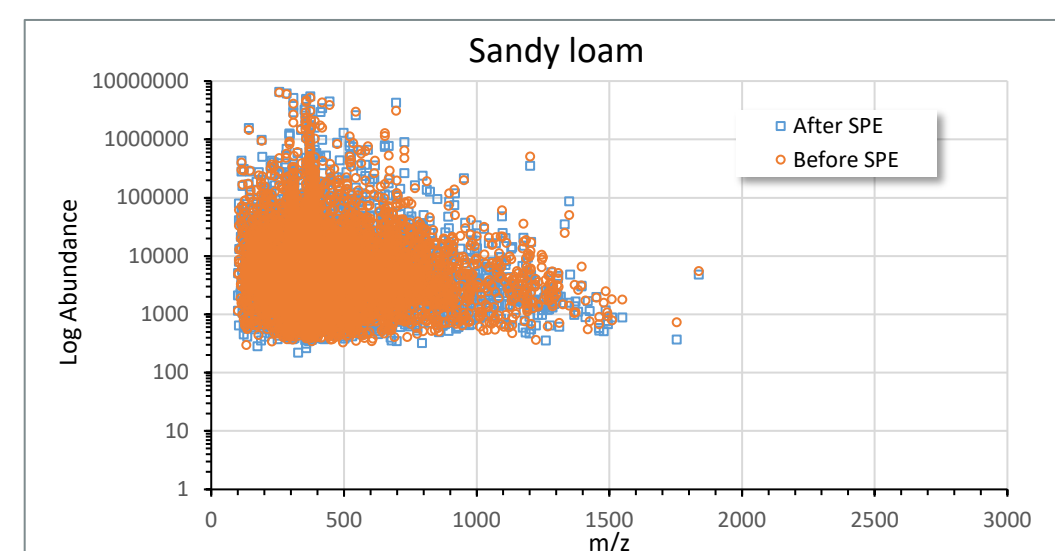
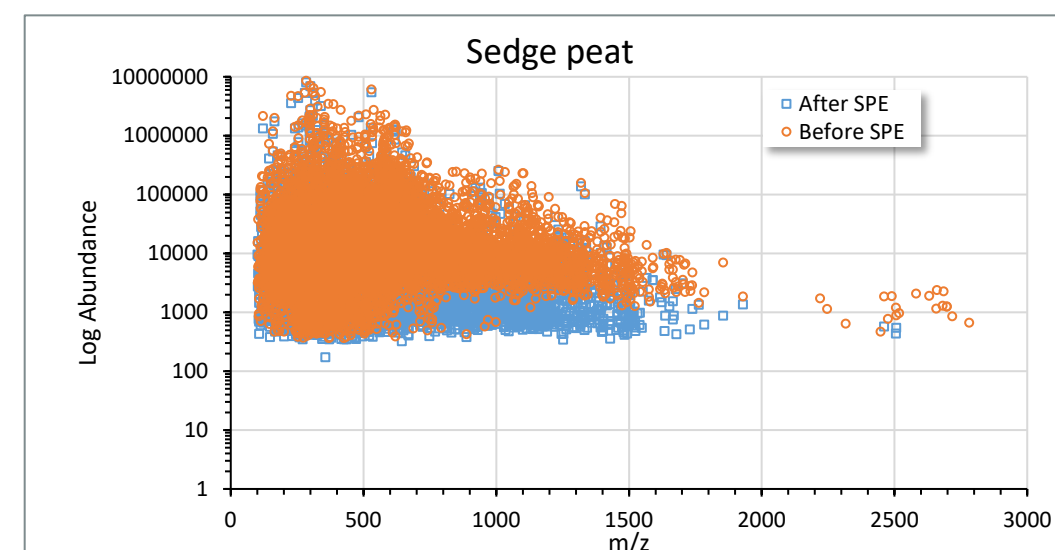
The figures below show the appearance of the extracts before and after passing over the Bond Elut Carbon cartridges. As expected, some of the pigments in the sedge peat extract are removed by the carbon. For the sandy loam, not much difference can be seen between the two samples.



Results and discussion

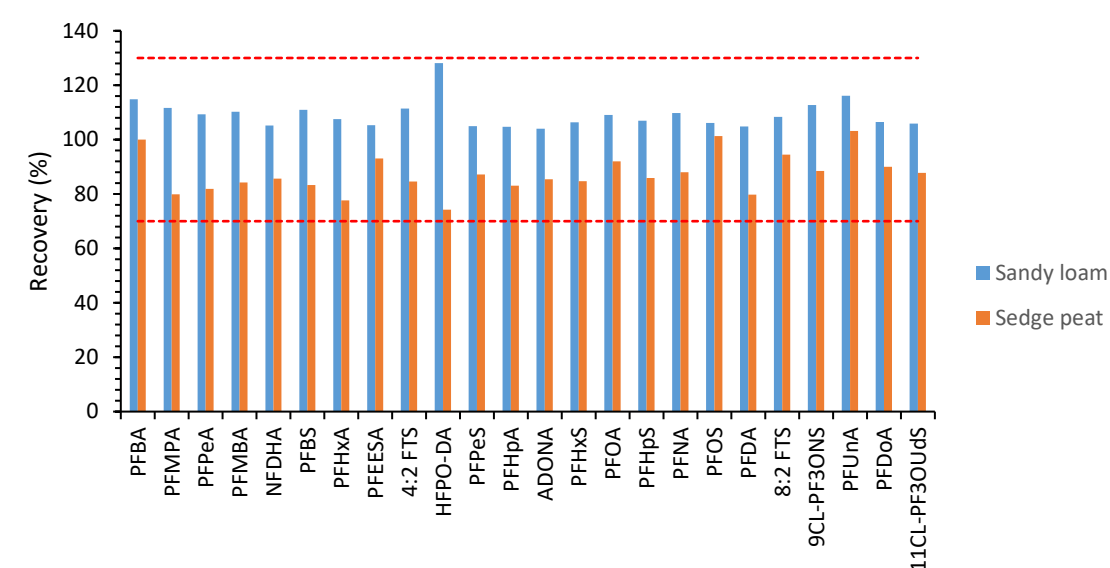
QTOF feature comparison

MassHunter Profinder was used to compare the extracts before and after cleanup with Bond Elut Carbon. The graphs below show the molecular features extracted with Q-scores of 100. The sedge peat has greater abundance of features from m/z 1000 to 1500 and a greater number of features from m/z 1500 to 2700 compared to the sandy loam. Interestingly, the sedge peat shows a reduction in the abundance of the features from m/z 600 to 2000 and elimination of most features from m/z 2200 to 2700 after SPE extraction. It is hypothesized that a subset of these features are responsible for the pigments observed in the extract solution.



PFAS recovery in matrix spikes

Each matrix was spiked with 25 PFAS standards at 1000 ng/L and extracted following the protocol, as shown. The graph below shows the calculated recovery of 24 of the compounds (excluding 6:2 FTS). The hashed red lines indicate common acceptance threshold between 70 and 130%.



Conclusions

Bond Elut Carbon for the cleanup of sedge peat shows a reduction in pigment of the extract solution and an associated reduction in molecular features. Recovery of matrix spiked PFAS compounds were within 70 to 130% for both sandy loam and sedge peat.